

Summary Abstract: Kinetics and mechanism of formic acid decomposition on Ru(001)

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The steady-state rate of decomposition of formic acid on Ru(001) has been measured as a function of surface temperature, parametric in the pressure of formic acid. The products of the decomposition reaction are CO₂, H₂, CO, and H₂O, i.e., both dehydrogenation and dehydration occur on Ru(001). A similar product distribution has been observed on Ni(110),¹ Ni(100),² Ru(100),³ Fe(100),⁴ and Ni(111)⁵ surfaces; whereas only dehydrogenation to CO₂ and H₂ occurs on the Cu(100),⁶ Cu(110),⁷ and Pt(111)⁸ surfaces. Only reversible adsorption and desorption of formic acid is observed on the less reactive Ag(110) surface at low temperatures,⁹ whereas the more reactive Mo(100) surface is oxidized by formic acid at low temperatures with the products of this reaction being H₂, CO, and H₂O (Ref. 10). We report here the confirmation of earlier observations of the occurrence of both dehydrogenation and dehydration of formic acid on Ru(001),^{11,12} and more importantly, we provide a detailed mechanistic description of the steady-state decomposition reaction on this surface in terms of elementary steps.

Details concerning both the UHV system that was employed in this work¹³ as well as crystal preparation and cleaning¹⁴ have been presented previously. The formic acid was introduced onto the Ru(001) surface through a directional beam doser consisting of a multichannel array of capillaries, and the ratio of the "beam pressure" of formic acid at the surface when the crystal was in front of the doser to the background pressure of formic acid in the UHV chamber was > 40. Under our experimental conditions, the incident formic acid was predominantly in monomer form. The rate of decomposition of the formic acid was measured by a multiplexed quadrupole mass spectrometer (UTI-100C) as the Ru(001) surface was positioned in and out of the formic acid beam with the surface temperature held constant. The measurements were carried out at surface temperatures between 350 and 800 K and for formic acid pressures of 7.3×10^{-7} and 2.1×10^{-6} Torr.

Arrhenius plots of the rate of decomposition of formic acid on Ru(001) are shown in Fig. 1 from which it is clear that there are two quite distinct kinetic regimes, labeled I and II in the figure. At relatively low surface temperatures between 360 and 400 K (regime II), the reaction rate is zero order in formic acid pressure with apparent activation energies of 16.0 ± 0.3 kcal/mol for CO₂ and H₂ production, and 15.0 ± 1.0 kcal/mol for CO and H₂O production. At temperatures above 500 K (regime I) the reaction rate becomes first order in formic acid pressure with apparent activation energies of -1.3 ± 0.2 kcal/mol for CO₂ and H₂ production, and -0.2 ± 0.3 kcal/mol for CO and H₂O produc-

tion. The logarithm of the ratio of the rate of production of CO₂ and H₂ ($\equiv R_{\text{CO}_2}$) to that of CO and H₂O ($\equiv R_{\text{CO}}$) is plotted as a function of reciprocal surface temperature in Fig. 1(b). It is apparent that the rate of dehydrogenation is two to three times greater than that of dehydration in regime II, and five to eight times greater in regime I.

The kinetics of dehydrogenation of DCOOH were measured and compared with those of HCOOH. They are essentially the same in regime I. At relatively low temperatures (regime II), however, the apparent activation energy for DCOOH is 17.1 ± 0.3 kcal/mol, compared to 16.0 ± 0.3 kcal/mol for HCOOH. The absolute rate of dehydrogenation of HCOOH in regime II is greater than that of DCOOH.

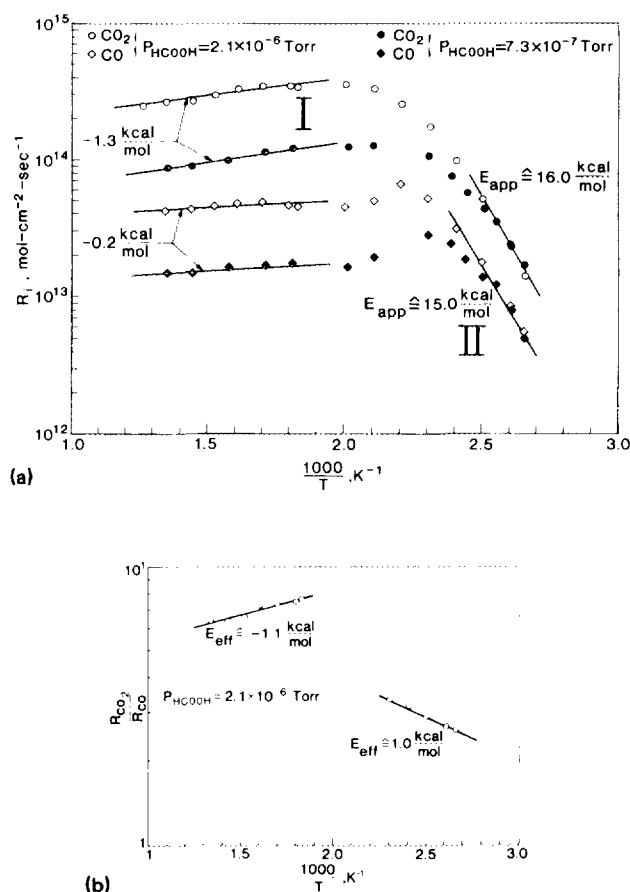


FIG. 1. (a) Arrhenius plots of the steady-state rate of decomposition of formic acid on Ru(001). Note that the reaction is zero order below ~ 400 K and first order above 500 K. (b) Logarithm of $R_{\text{CO}_2}/R_{\text{CO}}$ as a function of reciprocal temperature.

This difference in the kinetics of dehydrogenation of DCOOH and HCOOH is due to a kinetic isotope effect, and indicates that C–H bond cleavage is involved in the rate-limiting step under these conditions. A third kinetic regime (regime III, not shown in Fig. 1) was observed below 370 K for the dehydrogenation of DCOOH. The rate is zero order in formic acid pressure in regime III with an apparent activation energy of 29.0 ± 0.6 kcal/mol.

A bidentate formate species has been identified by electron energy-loss spectroscopy to be the stable intermediate upon adsorption of formic acid on Ru(001) at 90 K with subsequent annealing to between 200 and 375 K.^{11,12} Chemisorbed carbon monoxide and oxygen adatoms were observed spectroscopically on the surface after annealing to higher temperatures. The observation of the isotope effect for C–H bond cleavage together with the fact that formate is a stable intermediate clearly indicate that formate decomposition is the rate-limiting step in kinetic regime II.

Additional insight into the reaction mechanism can be gained if one has knowledge of the coverages of the various surface species during the steady-state reaction. Transient thermal desorption measurements carried out during the steady-state reaction¹⁵ allow the determination of DCOO, D, H, and CO coverages during the steady-state decomposition of DCOOH. For pressures of DCOOH near 10^{-6} Torr, the hydrogen coverage is much smaller than that of deuterium in kinetic regimes II and III. Furthermore, the thermal desorption spectra of D₂ and CO₂ from DCOOH adsorbed at 300 K have the same shape and peak temperature. These facts imply that the formation of D₂ and CO₂ are governed by the same rate-limiting step, the decomposition of surface formate. The evolution of D₂ is reaction limited, whereas that of H₂ is desorption limited. The formate coverage (and thus the D coverage) remains essentially constant in kinetic regime III and decreases with increasing temperature in regime II with an activation energy given by $k_B d(\ln \theta_{\text{DCOO}})/d(T^{-1}) = -13.3 \pm 1.0$ kcal/mol ($\equiv E_{\theta_{\text{DCOO}}}$). The activation energy E for the elementary reaction $\text{DCOO(a)} \rightarrow \text{CO}_2(\text{g}) + \text{D(a)}$, the apparent activation energy of dehydrogenation E_{app} , and $E_{\theta_{\text{DCOO}}}$ are related by $E_{\text{app}} = E - E_{\theta_{\text{DCOO}}}$. Since $E_{\theta_{\text{DCOO}}} \approx 0$ in regime III, the apparent activation energy measured in this regime is the reaction barrier for formate to decompose via C–D bond cleavage ($E = E_{\text{app}} = 29.0 \pm 0.6$ kcal/mol). Utilizing the value $E_{\text{app}} = 17.1 \pm 0.3$ kcal/mol from regime II yields $E = 30.4 \pm 1.3$ kcal/mol, which agrees well with the value obtained from regime III (29.0 ± 0.6 kcal/mol). These results together with the kinetic isotope effect observed in regime II imply that the rate in regime III is also limited by the decomposition of formate.

The fact that the dissociative chemisorption of formic acid is irreversible was confirmed by reacting a mixture of HCOOH and D₂ of which the molar ratio was 1:2 and observing no mass 47 (HCOOD) as a reaction product under any conditions. The important fact that a secondary reaction leading to CO₂ via the oxidation of CO does not occur was established by carrying out the decomposition reaction at 500 K on a Ru(001) surface on which a half-monolayer of

¹⁸O was predosed. The only initially observed reaction products were H₂, C¹⁶O¹⁶O, and H₂¹⁸O. As the ¹⁸O was depleted from the surface, C¹⁶O was also observed as a reaction product; in no case was C¹⁶O¹⁸O detected, ruling out the secondary oxidation of CO on Ru(001) during the steady-state decomposition of formic acid.

The transition region separating kinetic regimes I and II occurs between approximately 425 and 475 K, and it is characterized both by the desorption of chemisorbed CO from Ru(001) and by the accumulation of oxygen adatoms on the surface. Auger electron spectroscopic data revealed that the concentration of oxygen adatoms is negligible below 425 K during the steady-state reaction, and approaches a quarter-monolayer as the temperature increases above 475 K. The presence of oxygen leads to an enhancement in the rate of production of CO₂ relative to CO.

To summarize, for formic acid pressures near 10^{-6} Torr, there are three distinct kinetic regimes in the steady-state decomposition reaction on Ru(001): regime I above 500 K, regime II between 360 and 400 K, and regime III below 370 K. At relatively low surface temperatures (regimes II and III) the rate is limited by the decomposition of surface formate; whereas at high temperatures, the rate is limited by the formation of formate from molecularly adsorbed formic acid. The low-temperature regimes are characterized by a Ru(001) surface that is essentially saturated with reaction intermediates. The coverage of CO remains approximately constant in regimes II and III and decreases above 425 K. The formate coverage is relatively constant in regime III and decreases rapidly in regime II. The surface hydrogen coverage is insignificant compared to those of CO and formate. The high-temperature regime is characterized by a surface on which there is a steady-state concentration of oxygen adatoms approaching a quarter-monolayer. The latter selectively enhances the rate of dehydrogenation (CO₂ and H₂ production) relative to dehydration (CO and H₂O production). A detailed account of this work, including mechanistic modeling, will be presented elsewhere.¹⁶

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